10/031232
531 Rec'd PCT/PTO 17 JAN 2002

1/PRTS

19036.3

Translation of PCT/EP00/06881 as filed on July 19, 2000

BACKGROUND OF THE INVENTION

Method for Producing a Composite Material, Composite Material Produced According to Said Method, Molded Part That Consists of Such a Composite Material and Method for the Production Thereof

The invention concerns a method for producing a composite material from a particulate foam that consists of a thermoplastic material and at least one layer connected thereto by heating the pre-foamed particles to a temperature in the region of the melting temperature and simultaneously or subsequently connecting to the layer. The invention also concerns a composite material produced with this method, that consists of a particulate foam and at least one layer connected thereto, molded parts made from such a composite material, and also methods of producing same.

Thermoplastic materials and plastic foams produced therefrom by expansion, especially particulate foams, are used for various applications. Plastic foams are mainly used as insulating heat, sound or impact layers and for reducing weight compared to compact materials. However, they absorb forces only to a limited degree and are usually neither abrasion-resistant nor diffusion-tight. In most applications, the plastic foam must therefore be coated at least on one

side or be totally covered, wherein the coating or covering material must provide a surface that is e.g. smooth, if necessary decorative, abrasion-resistant or sealing in dependence on the application, and/or should enhance the solidity of the molded part. Towards this end, the coating or covering material can e.g. be fiber-reinforced. Such composite materials are used in technical components, such as panel pieces in automobile technology, for housings, packings or the like.

After production and molding of the plastic foam of such composite materials, the plastic foam is e.g. connected to a cover layer by means of adhesives, solvents, etc. Alternatively, the cover layer is prefabricated and subsequently back-foamed with the foam particles. The first method is expensive and usually harmful to the environment and stresses can lead to delaminations. If the plastic foam and the cover layer consist of different polymers, the connection between cover layer and plastic foam is often inadequate. The cover layer can delaminate or crack under excessive stress thereby disintegrating the plastic foam or even decomposing the foam structure.

Composite materials of polyurethane foams are known having coated, e.g. laminated or glued, decorative sheets of polyurethane or polyvinyl chloride (PVC). Due to their thermosetting plastic properties, polyurethanes can disadvantageously be recycled to only a limited degree and for that reason must be either thermally recycled or be

granulated using demanding and expensive methods. This granulated matter is then often used for the fabrication of low-quality products. If the decorative sheet consists of PVC, recycling is even more difficult because of the variety in grades. Thermal recycling is also problematic due to the chloride content. Thermal utilization of plastic materials containing PVC produces polychlorinated dibenzodioxins and furans. An example thereof is the 2,3,7,8-tetrachlorodibenzodioxin, known as "toxin of Seveso", that has the highest toxicity of all currently known organic compounds.

DE 37 22 873 describes a method for producing a piece of equipment, in particular a panel piece for automobiles, comprising a thin-walled support layer, an intermediate layer and a decorative layer. The support layer is melted to the plastic foam, and the decorative layer is pressed onto the plastic foam, preferably by flame lamination, or is coated in a conventional fashion. The plastic foam consists of polyethylene, and the support layer consists of sheet metal or of a fiber mat containing polypropylene, or of a fiber glass material containing polypropylene. Polyolefin foams have poor thermal shape stability, being stable in shape only up to approximately 100°C to 110°C. This is insufficient for many molded parts that are e.g. exposed to sunlight, hot air or exhaust heat. This is particularly true for the automobile industry which requires thermal shape stability up to a temperature of at least 120°C.

DE 41 41 113 A1 discloses a composite body in the form of an automobile panel piece that consists of a polyolefin particulate foam and a decorative layer, also consisting of polyolefin polymers, which is laminated thereon. The decorative layer has a multilayer knitted fabric or tissue with embedded spacers of polymer fibers and has a decorative textile surface. Alternatively, the decorative layer is coated with a laminated sheet based on olefin polymers. This composite material is pure in grade but also has poor thermal shape stability.

It is the underlying object of the invention to provide a method of producing an environmentally friendly composite material with a tight bond between the particulate foam and the layer that is linked therewith, and with a higher heat resistance and resistance to thermal shock. The object also includes such composite materials, molded parts from such a composite material and methods for producing such molded parts.

SUMMARY OF THE INVENTION

This object is achieved in accordance with the invention by using a particulate foam of polyalkylene terephthalate, or of a polyalkylene terephthalate blend, with a low crystallite portion in an otherwise amorphous phase, and tempering the particulate foam, during production of the molded body, during bonding with the layer and/or subsequently and at a temperature at which the amorphous phase is converted into a higher crystallite portion.

JP 20 73 836 A discloses introduction of foamed particles together with granulated matter, made from a polymer having a low melting point, into an extruder and controlling the temperature of the extruder such that only the granulated matter is melted. The blend of molten polymer and foamed particles is then transferred to an injection mold. The molded body consists of a polymer matrix with embedded foamed particles. PET is mentioned along with a plurality of other polymers. No selection criteria is given.

The invention makes use of the improved thermal stability and resistance to thermal shock of the polyalkylene terephthalates, in particular of PET, which have melting points in the region of 250°C and softening points in the region of 200°C. However, these relatively high temperatures for the production of the molded body from the particulate foam require a correspondingly high energy input. For the conventional production of molded bodies using superheated steam, a steam pressure of more than 16 bar would be needed. The required energy input is therefore considerable. The mold device must be correspondingly constructed to provide it with the required tightness under pressure, especially at the separation location. The molding tools must have a corresponding wall thickness which increases not only the investment costs but also the energy demand due to the high heat capacity of the mold. Practical tests have shown that approximately 95 % of the energy input is used for heating the mold. This prevents economic production of the molded parts.

According to the inventive method, the foamed or pre-foamed polyalkylene terephthalate is used in a configuration with low crystallite portion in an otherwise amorphous phase with the softening temperature of said polyalkylene terephthalate being considerably lower than the softening temperature of polyalkylene terephthalates in conventional applications. However, such a polyalkylene terephthalate of low crystallite portion does not have the material properties that are desirable for the finished molded body or molded part. It has turned out that the crystallite portion of the amorphous phase can be considerably increased by tempering the particulate foam molded body during or after production so that the particulate foam in the composite material exhibits the usual desired properties. In this fashion, the particles can be linked using less energy and at reduced investment cost. Conventional molding machines can also be used for the processing of particulate foams from polyalkylene terephthalates.

If the molded body is formed from the particulate foam with pressurized superheated steam, the pressure and the pressurizing time can be controlled for tempering the particulate foam.

It is also possible to continue tempering the composite material after production of the molded body, e.g. by slow and/or controlled cooling using the heat within the molded body. In particular, the composite material can be removed

from the mold immediately after having reached the necessary natural stability at the surface, and then slowly cooled.

The temperature control that is necessary for producing as high a crystallite portion as possible can be effected using a conventional DSC-measurement during the process or with prototypes.

A composite material from a molded body of a particulate foam with at least one layer linked to the molded body, that is produced according to the inventive method is characterized in that the particulate foam consists of a polyalkylene terephthalate or a polyalkylene terephthalate blend.

The polyalkylene terephthalate particulate foam of the composite material according to the invention has extraordinarily high tensile and shear strength. Compared to other particulate foams, in particular the most common polystyrene foams, it is characterized by its high restoring force which prevents permanent compression points. It has a higher thermal shape stability than polyolefin particulate foams and is stable up to at least 120°C. Polyalkylene terephthalates, such as polyethylene terephthalates (PET), polypropylene terephthalates, polybutylene terephthalates, poly(1,4-cyclohexane dimethylene terephthalate)s etc. are thermoplastic polymers of high solidity, rigidity and shape stability, with good sliding and wear properties as well as high chemical resistance. Due to the thermoplastic properties, the polyalkylene terephthalate particulate foam

can be easily recycled and is therefore environmentally friendly. Even thermal disposal thereof does not produce toxic halogenated hydrocarbons.

The particulate foam consists preferentially of PET. Due to the partially crystalline structure of its molecular chains, PET has a particular high solidity and density (D ≈ 1,38 g/cm^3) and a high melting point of approximately 260°C. The partially crystalline structures and hence the material properties of PET can be modified by copolymerization with higher terephthalic acid esters or e.g. isophthalic acid.

To increase the solidity and especially the viscosity of the composite material, the particulate foam can have synthetic and/or natural reinforcing fibers, such as glass, metal, carbon, aramide, wood, cellulose, hemp fibers etc. These reinforcing fibers are preferentially arranged between and within the particles.

The composite material according to the invention can be produced as sheets or as a three-dimensional molded part, if necessary also as a hollow body, e.g. by molding the composite material onto a core. The composite material according to the invention is therefore especially suited for molded articles for internal panels, engine compartments and car body parts, e.g. inner door panels, sun visors, consoles, dashboards, cockpit modules, linings of engine compartments, bumpers, hoods, front end supports, ~~etc., for~~ furniture, particularly garden furniture, sports equipment, such as

surfboards, wave boards, hulls, for packagings, insulation boxes or housings or for model construction.

Depending on the application of the finished molded part, the layer that is connected to the particulate foam is designed as a visible decorative layer which gives the composite material a smooth or structured, decorative surface and an improved splash, scratch and abrasion resistance. The cover layer can consist e.g. of at least one thermoplastic polymer, e.g. a polyolefin sheet to provide the composite body with a smooth surface. The cover layer can e.g. also have a textile structure, in order to give the composite body the desired optical and haptic features and e.g. a surface structure, in particular for inside panel pieces for automobiles.

In a preferred embodiment, the cover layer consists of polyalkylene terephthalate, especially PET, or a polyalkylene terephthalate blend. In this case, the composite material according to the invention can be completely recycled due to its grade purity and its thermoplastic properties and is therefore environmentally friendly. On the other hand, the particulate foam and the cover layer form a solid and durable connection due to the compatibility of identical or similar polymers.

In accordance with a preferred embodiment variant, the cover layer is welded to the particulate foam or is laminated onto the particulate foam, e.g. flame laminated, calendered, coated, etc. As already mentioned, the cover layer can be

formed by a deep drawn sheet consisting of polyalkylene terephthalate.

In a preferred version, the cover layer is applied onto the particulate foam via an intermediate layer of fibers, wherein the intermediate layer preferably has a fiber mat. The intermediate layer can also be a tissue, knitted fabric, cloth, knits or the like.

Preferentially, the intermediate layer consists of polyalkylene terephthalate, in particular PET, or a polyalkylene terephthalate blend. To increase the strength of the composite material, the intermediate layer can be reinforced with synthetic and/or natural reinforcing fibers, such as glass, carbon, aramide, metal, cellulose, wood, hemp fibers etc.

The intermediate layer that is preferentially welded to the particulate foam, does not thermally affect the particulate foam during lamination of the cover layer. On the other hand, subsequent foaming of an intermediate layer that is preferably welded to the cover layer, prevents the particle structure of the particulate foam from becoming visible by pressing through the cover layer. Furthermore, such an intermediate layer produces comfortable and soft haptic features for the molded part made from the composite material which is desirable for many applications.

According to another preferred variant of the embodiment, the intermediate layer is a mixed fiber layer which contains a portion of polyalkylene terephthalate fibers, in particular PET, which are welded to the particulate foam, and a further portion of synthetic and/or natural reinforcing fibers which have sufficient wettability for at least one solidifying, hardening and/or linking polymer which forms the cover layer and is disposed in the liquid phase onto the free surface of the mixed fiber layer. The intermediate layer thereby serves two functions within the composite material: the conventional reinforcing function with respect to solidity and viscosity and also the bonding between the cover layer and the polyalkylene terephthalate particulate foam, since it contains polyalkylene terephthalate fibers which form a close welding connection therewith when melting the particulate foam. This produces a strong bond between the intermediate, mixed fiber layer and the particulate foam. The free surface of the intermediate layer also has sufficient wettability for applying or impregnating a solidifying hardening or linking polymer such that a coating having the required properties, e.g. smooth surface, abrasion resistance, resistance to splashing and scratches etc., is disposed on the composite of mixed fiber layer and polyalkylene terephthalate particulate foam. The coating of a solidifying, hardening or linking polymer which is disposed on the free surface of the mixed fiber layer can, for its part, comprise several layers, e.g. have a sandwich-like design.

The polymer which has been disposed in the liquid phase onto the free surface of the mixed fiber layer can e.g. be a thermoplastic material disposed on the mixed fiber layer using any conventional method, such as injection molding or low-pressure injection molding, pressing on, extrusion or coextrusion, thermoplastic foam casting, thermal molding, flame injection, extrusion deposition or extrusion flow methods. The thermoplastic material, e.g. polyolefines, polystyrene, polyacrylates etc., which is transferred into the liquid molten phase by heating, solidifies during cooling on the mixed fiber layer, wherein this layer serves not only as a bonding agent and a reinforcement but, in particular, also as a heat insulation layer which thermally protects the particulate foam during injection, extrusion or the like.

The thermoplastic material polyalkylene terephthalate, in particular PET, disposed in the liquid phase is preferably such that the composite material is characterized by good thermal stability and high purity of grades as well as low material and production costs.

The polymer disposed in the liquid phase can also be a linking polymer in the form of an elastomer, e.g. caoutchouc. An elastomer provides additional functions in the surface region, such as improved grip, dampening of pressure and impact forces.

It is also possible to dispose a linking polymer in the form of a thermosetting plastic material onto the free surface of

the mixed fiber layer. The thermosetting plastic material can be disposed - like the elastomer - in any fashion, e.g. by slush techniques, soaking, impregnation, spraying or reaction injection molding (RIM or RRIM=reinforced reaction injection molding or SRIM=structural reaction injection molding) which is based on rapid admixing and blending of the liquid thermosetting components, injection of the reactive mixture onto the mixed fiber layer and rapid hardening. Liquid monomers or oligomers with integrated powdery polymers can be used, wherein these act like crystallization seeds during hardening or linking of monomers or oligomers on the mixed fiber layer, wherein the hardened and/or linked polymer has a low polymerization loss due to the portion of already polymerized particles. When thermosetting plastic materials or elastomers are used, the mixed fiber layer also acts as a heat insulation layer in order not to impair the particulate foam during the usually exothermal linking. Essentially all known thermosetting plastic materials can be used, e.g. polyurethane, epoxy, melamine, urea, formaldehyde or phenolic resins and compounds of these resins.

To improve the strength of the inventive composite material, the polymer which has been disposed in the liquid phase onto the free surface of the mixed fiber layer, can be reinforced with synthetic and/or natural fibers.

The polymer disposed in the liquid phase onto the free surface of the mixed fiber layer can also comprise a decorative layer, e.g. a sheet, textile or the like, at least

on the visible side, which can be disposed in any conventional fashion onto the solidified, hardened and/or linked polymer or at the same time when the liquid polymer is disposed onto the mixed fiber layer. The decorative layer can e.g. also be a sheet of veneer, e.g. wooden veneer which is glued onto the smooth surface of the solidified, hardened and/or linked polymer.

In a further development of the inventive composite material, at least one supporting layer is disposed on at least one free surface of the particulate foam or inside the particulate foam. The supporting layer preferably comprises at least one compact insertion part, e.g. a supporting element in the form of an injection molded part. It preferably consists of a compact polymer and also preferably contains polyalkylene terephthalate, in particular PET or is completely formed thereof. The supporting layer is preferably welded to the particulate foam. In this case, the supporting layer which consists of compact material imparts the largest possible stability and durability to the composite material, while the particulate foam serves e.g. as an impact, sound or heat insulation layer and reduces the weight of the composite material. If the composite material comprises a cover layer, as mentioned above, this cover layer provides a smooth or structured surface and improved resistance to scratching and abrasion.

The invention also concerns molded parts which consist essentially of a composite material of the above-mentioned

structure, and methods for producing such molded parts. An embodiment of such a method provides that densely packed particles of polyalkylene terephthalate having a low crystallite portion which is foamed and/or prefoamed and provided with a foaming agent, are heated in a mold to a temperature at which the surface of the particles melt, and connected into the molded body, and after cooling at least one layer, e.g. a cover layer, is laminated onto at least one free surface of the particulate foam molded body, and the particulate foam molded body is tempered during its production and/or during cooling through corresponding temperature control. The term "mold" designates herein any molding measure producing plate-shaped, spatial or hollow molded parts.

The densely packed polyalkylene terephthalate particles are heated to a temperature at which only the surface of the particles melts and interconnects. After cooling of the foamed body, the smooth or textiled cover layer, which consists in particular of thermoplastic polymers, e.g. polyalkylene terephthalate, is laminated by means of any technique, e.g. by flame lamination, deep drawing or the like. In a preferred embodiment, the particles are heated in the presence of a textile intermediate layer, e.g. a fleece of polyalkylene terephthalate, at which the surface of the particles melts, and the intermediate layer is foamed, the composite obtained is cooled and the cover layer is then laminated onto the intermediate layer. This ensures that during lamination of the cover layer, the particulate foam is

not thermally impaired and e.g. if the cover layer is a thin sheet, the foamed particles are not visible through the cover layer. This intermediate layer also produces soft haptic features.

In another method variant for producing a molded part from such a composite material at least one layer, e.g. a cover layer, and densely packed particles of foamed polyalkylene terephthalate or pre-foamed polyalkylene terephthalate provided with a foaming agent are heated in a mold to a temperature at which at least the surface of the particles melts, the cover layer is back-foamed, and the composite material is subsequently cooled. In this case as well, an intermediate layer, e.g. a fleece of polyalkylene terephthalate can be preferably disposed between the particles and the cover layer, and the intermediate layer can be preferably welded to both the cover layer as well as to the particulate foam during subsequent foaming thereof. The foaming produces a lasting connection among the layers wherein the one-step method guarantees rapid and inexpensive production of the inventive composite material. Alternatively, the intermediate layer can be initially connected to the cover layer, e.g. by welding with subsequent back-foaming of the intermediate layer.

In another method for producing a molded part from an inventive composite material, an intermediate layer in the form of a mixed fiber layer containing a portion of polyalkylene terephthalate fibers, in particular PET, and a

further portion of reinforcing fibers having sufficient wettability for a polymer in liquid phase forming the cover layer, and densely packed particles of foamed polyalkylene terephthalate and/or polyalkylene terephthalate having at least one foaming agent which disintegrates in the region of the melting temperature of the polyalkylene terephthalate, are heated in a mold to a temperature at which the surface of the particles and the polyalkylene terephthalate fibers of the mixed fiber layer melt, the obtained composite is subsequently cooled and the solidified, hardened and/or linked polymer is disposed in the liquid phase onto the free surface of the mixed fiber layer. Since the intermediate, mixed fiber layer contains polyalkylene terephthalate fibers, these fibers are melted thereby producing a strong material link between the mixed fiber layer and the particulate foam. As mentioned above, a molten thermoplastic material or a hardening or linking polymer (elastomer or thermosetting plastic material) is subsequently disposed in the liquid phase onto the mixed fiber layer using any conventional technique and the desired molded part is obtained after solidification, hardening, or linking. The solidifying, linking or hardening polymer can e.g. connect two molded parts.

Alternatively, the cover layer can be prefabricated, e.g. the mixed fiber layer can be impregnated with the solidifying, hardening and/or linking polymer. Care should be taken that the polymer does not protrude through to the other side of the mixed fiber layer. The foamed particles are then disposed

onto the free surface of the mixed fiber layer and heated thereby simultaneously producing a strong connection to the polyalkylene terephthalate fibers of the mixed fiber layer.

In one embodiment, the solidifying, hardening and/or linking polymer is mixed in the liquid phase with synthetic and or natural reinforcing fibers and subsequently disposed onto the free surface of the mixed fiber layer. If the polymer is e.g. a thermoplastic material which is extruded onto the mixed fiber layer, the reinforcing fibers can be added to an extruder in the region of the extruder screw at which the thermoplastic material is substantially completely plastified. The reinforcing fibers can be added to the liquid polymer in any fashion irrespective of whether the polymer is a thermoplastic material, an elastomer or a thermosetting plastic material.

A decorative layer, e.g. a sheet, textile or the like can be optionally disposed on the visible side of the polymer disposed in the liquid phase. In a preferred embodiment, the decorative layer is simultaneously disposed onto the mixed fiber layer together with the polymer by injection, compression or the like. In this fashion, the polymer can be disposed in the liquid phase onto the composite consisting of particulate foam and mixed fiber layer in that the composite and the decorative layer are disposed in a mold and the liquid polymer which is optionally reinforced by fibers is introduced between composite and decorative layer using any conventional method. The smooth surface of the solidified,

hardened or linked polymer can then be easily provided with a decorative layer, e.g. having a glued-on wooden veneer.

All above methods permit heating the particles in the mold in the presence of a compact supporting layer to a temperature at which at least the surface of the particles melts, and foaming up of the support. The supporting layer preferably consists of a polymer or a polymer blend, e.g. of substantially compact polyalkylene terephthalate, such as PET.

The particles and optionally the cover layer and/or the intermediate layer can be heated to the melting temperature by means of a gas phase diffusing same, e.g. hot vapor. The diffusion-open structure of the layers leads to an intimate bonding of the particulate foam as well as among the layers.

Alternatively, the particles and optionally the cover layer and/or the intermediate layer and/or the supporting layer can be heated to the melting temperature using microwave energy, wherein a medium which absorbs microwaves, such as water, alcohol or the like, can preferably be used. The microwave-absorbing medium can be disposed e.g. in the liquid phase onto the surfaces to be connected and be removed from the mold after evaporation. In this fashion, the type and amount of the microwave-absorbing medium used produces a reliable welding connection and prevents local overheating in the mold.

INS A1 >

Embodiments of the invention are explained in detail below with reference to the drawing.

Fig. 1 shows a cross-section of a molded part having the shape of a sports device produced from a composite material in accordance with the invention;

Fig. 2 shows a cross-section of a molded part in the shape of a lining part for the interior of automotive vehicles produced from a composite material in accordance with the invention.

INS A2 >

The molded part 5a shown in Fig. 1, e.g. a surf board, comprises a compact support layer 1 which can consist e.g. of PET or of a blend of PET and other polyalkylene terephthalates. A particulate foam 2 surrounds the support layer 1 which e.g. also consists essentially of PET or of a blend of PET and other polyalkylene terephthalates and which is preferably welded to the support layer to produce a tight connection between the support layer 1 and particulate foam 2. An intermediate layer 4, i.e. a layer of mixed fibers, is disposed on the particulate foam having a portion of polyalkylene terephthalate fibers which are welded to the particulate foam 2. The mixed fiber layer also comprises reinforcing fibers, e.g. glass or carbon fibers which have sufficient wettability for a rigidified, hardened, or linked polymer, e.g. polyurethane, disposed in the liquid phase onto the free surface of the mixed fiber layer to form a cover layer 3. The cover layer 3 provides high diffusion tightness,

resistance to spraying, scratching and abrasion. It can also have a sandwich-like design of several superposed layers.

Fig. 2 shows a molded part 5b of uniform material, e.g. a dashboard 7 of an automotive vehicle including instrument housing 6. The molded part 5b consists e.g. of a PET particulate foam 2 and a decorative cover layer 3 of PET disposed on its visible side. The cover layer 3 can be e.g. in the form of a textile, such as a tissue, knitted fabric or the like. An intermediate layer 4 disposed between particulate foam 2 and cover layer 3, which consists e.g. of a PET fleece gives the molded part 5b soft haptic features. If the cover layer 3 is laminated onto the particulate foam 2, the intermediate layer 4 provides additional thermal protection for the particulate foam 2 when applying the cover layer 3. If the intermediate layer 4, which is e.g. welded to the cover layer 3, is subsequently back-foamed with the particulate foam 2, penetration of the particulate foam 2 through the visible surface of the cover layer 3 is prevented.